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II.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

A REVISION OF THE ATOMIC WEIGHT OF BARIUM.

SECOND PAPER: THE ANALYSIS OF BARIC CHLORIDE.

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Presented May 10, 1893.

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Introduction.

During the time occupied by the recent investigation of baric bromide,* similar analyses of baric chloride were being made. The problem involved was far more complicated than the one already published, because of the solubility of argentic chloride in water; hence the present paper, which might well have come first, was necessarily postponed. The results of the continued investigation confirmed the high value of the atomic weight of barium, 137.43, obtained from the results of the investigation of baric bromide.

The balance and weights, and all the precautions relative to the weighings, have been already described in detail.† The remarks made before about the constancy of the weights, and the various comparisons with the Washington standard, naturally apply with equal force to the present work. At the close of the two years' investigation the weights were again compared, and were found to have remained surprisingly constant in relative value.

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* These Proceedings, XXVIII. 1. Zeitschr. Anorg. Chem., III. 441; IV. 160.

† Ibid., XXVI. 242; also XXVIII. 5.

The following atomic weights of various elements entering into the present research will be assumed throughout the paper:—

Oxygen = 16.000 Hydrogen = 1.0075
Bromine = 79.955 Silver = 107.930
Chlorine = 35.456 Sulphur = 32.065

PROPERTIES OF BARIC CHLORIDE.

The properties of baric chloride are so familiar as to need little further description.[*] The colorless flat tables of the rhombic system contain, as is very well known, two molecules of water together with the usual slight excess. Half of this water is given off at 60–65°,[†] and the rest at somewhat higher temperatures. All the water is regained at ordinary temperatures in ordinary moist air. According to Filhol[‡] the crystals possess a specific gravity of 2.66, while according to Joule and Playfair,[||] Schiff,[§] and Schroeder[¶] they possess a specific gravity of about 3.05. This great discrepancy is too serious to neglect, hence a redetermination was made.

The apparatus for the determination of the specific gravity was similar to that already described,[**] and toluol was again used as the liquid to be displaced. 5.701 grams (in air) of powdered crystallized baric chloride were found to displace 1.5864 grams of toluol at 24°, or 1.8408 grams of water at 4°. Hence the specific gravity sought is 3.097. The reason for at least a part of the discrepancy is undoubtedly to be found in the enclosure of varying amounts of mother liquor in the crystals.

The specific gravity of anhydrous baric chloride has been much more definitely determined. According to Quincke,[††] the value of this constant is 3.851 at 0°; according to Favre and Volson,[‡‡] it is 3.844 at 17°; and according to Schroeder,[§§] it is 3.879 at 4°. Although without doubt the mean of these values would have served the present purpose, a new determination was made, as much to check the previous determinations in the present research as to serve for the basis of reduction to vacuum.

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[*] See Graham Otto (Michaelis), III. 658; also Watt's Dictionary (Muir), I. 441, etc.

[†] Lescœur, Compt. Rend., CIV. 1511.

[‡] Graham Otto (Michaelis), *loc. cit.*

[||] Chem. Soc. Mem., II. 401; III. 57, 199.

[§] Annalen, CVIII. 21.

[¶] Jahresbericht 1879, p. 31.

[**] These Proceedings, XXVIII. 14.

[††] Graham Otto (Michaelis), III. 659.

[‡‡] Ibid.

[§§] Berichte d. deutsch. c. Gesell. 1878, 2131.

4.8620 grams (in air) of baric chloride which had been dried to constant weight at 220° were found to occupy the same volume at 24° as 1.2608 grams of water reduced to 4°. Hence the specific gravity of baric chloride under these conditions is 3.856, a value which agrees essentially with those given above.

Here, as in the case of baric bromide, the question whether the water of crystallization is absolutely expelled at a red heat is one of the greatest importance. All early experiments have assumed that this is the case, without attempting to disprove the contrary assumption. The first stumbling block in the way of the careful investigation of the problem is the decomposition of baric chloride in the air at high temperatures. Marignac's statement that the salt may be ignited at a dull red heat without the loss of a trace of chlorine * has not been confirmed by the present experience. As a matter of fact, baric chloride loses almost as much halogen as the bromide, upon gentle ignition in the air.† Hence in order to determine the true weight of baric chloride present in all those cases where the salt was ignited in this way, it was necessary to determine the amount of baric hydroxide and baric carbonate existing in the solution of the ignited salt. Pure boiled water which had been prepared solely in platinum was used for making this solution, and phenol phthaleïn and methyl orange were used as indicators. Of course, the loss of 0.00355 gram of chlorine would correspond to a correction of +0.00055 gram to the weight of the baric chloride if the alkaline earth were in the form of carbonate, +0.00185 gram if it were in the form of hydroxide, or +0.00275 gram if it were in the form of oxide. Since it is somewhat uncertain whether the portion which is determined by phenol phthaleïn really exists when dry in the form of hydroxide, and not in the form of oxide, the mean of the last two figures, 0.0023 gram, was adopted in the work which follows. In the case of baric bromide, this correction was calculated for the hydroxide. The corrections are in any case so very small that the possible error introduced by either method of procedure is quite unimportant. Another possible error of about the same magnitude is to be found in the fact that pure baric carbonate is not wholly without influence upon phenol phthaleïn.

In order to observe the behavior of baric chloride under gradually

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* Liebig's Annalen, LXVIII. 215; CVI. 165.

† Schultze, Journ. f. prakt. Chem., [2], XXI. 407.

increasing heat, specimens of very pure material were heated at many different temperatures by means of a Berzelius spirit lamp, and finally raised to redness. The residues were then dissolved in water and the alkalimetric corrections were determined and applied in the manner which has just been described. Below are given the experimental data.

(1.) 3.17+ grams of pure baric chloride which had been dried to constant weight (for twelve hours) at 260°± lost 0.27 milligram on heating to somewhat over 300°, 0.18 milligram more on heating to about 450°, and yet 0.30 milligram upon ignition at a medium red heat. To neutralize the baric hydroxide found upon dissolving the salt, about 0.4 cubic centimeter of the standard solution of hydrochloric acid was required. Since a cubic centimeter of this solution corresponded to a milligram of silver, it is evident that the correction to be added to the weight of baric chloride amounted to 0.09 milligram.

(2.) About 3 grams of baric chloride dried at 400° lost no weight on heating to redness. The alkalimetric correction was +0.12 milligram.

(3.) About 5.0 grams of baric chloride dried at 400° lost 0.17 milligram on heating to dull redness. The alkalimetric correction to be added to the weight of the baric chloride amounted to 0.12 milligram.

(4.) 5.46 grams of baric chloride dried at 250° lost 0.66 milligram on heating to dull redness, 0.22 milligram of this loss being accounted for by the alkalimetric correction.

(5.) A repetition of Experiment 4 showed a loss of 2.0 milligrams between 250° and dull redness, only 0.10 milligram of this amount corresponding to the alkaline earth found.

(6.) About 4.0 grams lost 1.20 milligrams between 300° and dull redness, the alkalimetric correction being only 0.06 milligram.

(7.) 2.61 grams of baric chloride dried at 300° lost 0.40 milligram upon being ignited to a bright red heat in a stream of nitrogen. 0.15 milligram of this loss was due to substitution of oxygen for chlorine.

(8.) 6.37 grams of baric chloride which had been dried at 200° lost 1.75 milligrams of water upon being heated to 300°±, and 1.30 milligrams more upon being partly fused at a bright red heat in a stream of nitrogen. The alkalimetric correction was +0.74 milligram.*

(9.) 3.6 grams of baric chloride dried at 300° lost 0.32 milligram upon being heated to dull redness, only 0.04 milligram being due to loss of chlorine.

(10.) 3.11 grams of baric chloride which had been prepared by drying large clear crystals at 160° lost 0.70 milligram on heating to dull redness. The alkalimetric correction was 0.29 milligram.

(11.) 2.65 grams heated to dull redness lost 0.17 milligram upon being further heated to bright redness. The alkalimetric correction was +0.25 milligram.

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* See page 77 of this paper.

(12.) 1.5 grams heated at 250° lost 1.0 milligram on fusion in a stream of dry pure hydrochloric acid gas. No trace of alkali or acid was found in the concentrated solution of the residue, but the addition of 0.10 cubic centimeter of hundredth normal hydrochloric acid made the neutral solution perceptibly acid to methyl orange.

(13.) 5.36 grams dried at dull redness lost no weight on fusion in hydrochloric acid at bright redness. The residue was wholly neutral.

(14.) 3.92 grams dried at dull redness lost 0.13 milligram on fusion in hydrochloric acid. The heat was so great that the crucible was attacked.

(15.) 4.28 grams of baric chloride dried at dull redness *gained* 0.23 milligram on partial fusion in hydrochloric acid. This specimen, as well as the previous one, was absolutely neutral.

ACTION OF HEAT ON BARIC CHLORIDE.

No. of Exp.	About 200°.	About 250°.	About 300°.	About 400°.	Dull Redness.	Bright Redness.	Fused in HCl.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
1		+0.021	+0.012	+0.006	–0.003		
2				–0.004	–0.004		
3				+0.001	–0.002		
4		+0.009			–0.004		
5		+0.038			–0.002		
6			+0.029		–0.002		
7			+0.014			–0.006	
8	+0.036		+0.009			–0.011	
9			+0.008		–0.001		
10	+0.013				–0.009		
11					–0.003	–0.010	
12	+0.066						0.000
13					0.000		0.000
14					+0.003		0.000
15					–0.005		0.000
Aver.	+0.038	+0.023	+0.014	+0.001	–0.003	–0.009	0.000

The foregoing table contains a summary of all the experiments, reduced to a common basis. Thus the column headed "Dull Redness" shows that on the average baric chloride ignited at about 500° or 600° loses three parts in one hundred thousand of its weight. The true weight of the baric chloride was computed in each case by adding the alkalimetric correction to the last weight taken; and then the percentage of excess or deficiency in weight was computed for each temperature and tabulated in its appropriate place.

The variations noticeable in the amounts of water retained at the lower temperatures are probably in great part due to the varying hygroscopic condition of the atmosphere at the time of drying, as well as to inaccuracies in the temperatures recorded.

There are necessarily three standards for determining the true weights of baric chloride forming the basis of the table above: one involves the weight of the salt ignited at dull redness plus the alkalimetric correction (Experiments 1, 2, 3, 4, 5, 6, 9, and 10); another involves the weight of the salt ignited at bright redness plus the same correction (Experiments 7, 8, and 11); and the third involves the weight of the salt fused in hydrochloric acid, without any correction (Experiments 12, 13, 14, and 15). A comparison of the results of Experiments 11, 13, and 15 with all the earlier experiments is sufficient to show that the three standards are very nearly, if not quite, identical; in other words, that baric chloride which has been dried at dull redness, or even at 400°, does not lose an essential amount of water upon being heated nearly to 900°. Nevertheless, below 400° — which is about the point at which the salt begins to show signs of partial decomposition — very noticeable amounts of water appear to be held by the so called anhydrous salt.

The conclusion regarding the expulsion of water from the baric chloride is so important that it seemed desirable to prove it in another way. Hence two determinations of the water of crystallization of perfectly homogeneous powdered pure baric chloride were made by two distinct methods: —

(16.) In the first case 3.10784 grams (in vacuum) of the powdered crystals were dried at a medium red heat by means of a spirit lamp to the constant weight of 2.64851 grams (in vacuum) and cooled in a vacuum over phosphoric anhydride. The solution of this salt required 1.00 c.c. of standard hydrochloric acid (of which the cubic centimeter corresponded to a milligram of silver) to render it neutral to phenol phthaleïn, and 0.85 c.c. more to reach the neutral point with regard to methyl orange.

Hence the alkalimetric correction is found to be 0.00025 gram, and after adding this weight to the observed weight of the dried salt, the true per cent of water present in the original crystals is found to be 14.7717.

(17.) Again, 5.02356 grams (in vacuum) of the same sample were dried in a platinum crucible at about 400° by means of the spirit lamp, and then fused in a stream of pure dry hydrochloric acid gas in a double crucible. The constant outflow of hydrochloric acid was sufficient to prevent the absorption of sulphuric acid from the products of the combustion of the illuminating gas, hence it was possible to use this source of heat. Indeed, the highest temperature obtainable by means of a powerful Bunsen burner is required to fuse the salt. After fusion, the salt was found to weigh 4.28148 grams (in vacuum), having lost 14.7720 per cent.

These results (14.7717 and 14.7720) agree within the limit of the probable experimental error; therefore very satisfactory confirmation is given to the conclusion arrived at before. Hence baric chloride is a compound of sufficient definiteness to form a very satisfactory basis for the determination of the atomic weight of barium.

The other properties of the salt — its solubility in water and insolubility in alcohol, the specific gravity of its solution, and so forth — have been studied by Gay Lussac, Gerlach, Karsten, Kopp, Mulder, and many others, and further remark upon them is unnecessary here.

Preparation of Materials.

Baric Chloride. — The ready crystallization of baric chloride upon the addition of alcohol to a strong aqueous solution of the salt furnishes an admirable method for the preparation of baric chloride in a pure state. This method of crystallization was freely resorted to in preparing the pure salt used in the preliminary experiments; but the details of the preparation need not be dwelt upon. The spectroscopic test of the purity of the salt has already been described at length.* The purest specimens of baric chloride used in the final experiments were prepared by three methods. According to the first of these methods, after the salt had been crystallized two or three times from water, it was precipitated five times in succession by the addition of strong pure hydrochloric acid to its concentrated aqueous solution. Each time the mother liquor was wholly discarded, and the crystals were carefully drained. The last precipitate was then dissolved in water, and reprecipitated twice successively by means of the purest alcohol. These and the subsequent operations were conducted in platinum vessels. A portion of the salt thus formed (I.a) was used for Analyses 22, 25, 31, and 32. The remainder of the crystalline powder was washed four times with pure alcohol on the filter pump, dried, ignited, and fused in a large platinum crucible. The translucent cake of anhydrous baric chloride was dissolved in the purest water, and the solution was allowed to stand until it had become neutral. After having been filtered from the baric carbonate, which was of a faintly brownish tinge because of the presence of impurity taken from the platinum during the fusion, the baric chloride was precipitated twice more by means of alcohol. The last crystals were dissolved in the purest boiling water, recrystallized by cooling, and finally washed once with cold water. The very pure salt thus formed was used for Analyses 20, 21, 33, and 35 (Sample I.c). The last mother liquor was freed from most of its salt by the addition of pure alcohol; and the very small amount of salt remaining in solution was recovered by the evaporation of the large volume of alcoholic solution and analyzed (Sample I.b, Analysis 34).

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* These Proceedings, XXVIII. 7.

The second chief specimen of baric chloride was treated in a different way. A large quantity of the commercially pure salt ("purissimum") was dissolved in water, and was then evaporated nearly to dryness with excess of pure hydrochloric acid on a steam bath, to decompose the thiosulphuric acid which is usually present. The hot dilute solution of the residue was treated with an excess of hydrogen sulphide, and the whole allowed to stand in the dark for a long time in a tightly corked stout flask. The clear supernatant liquid was siphoned off from the trace of precipitate and made alkaline with baric hydroxide which had been recrystallized six times.* After a suitable time the clear liquid was again decanted and filtered from the sulphides insoluble in the alkaline solution, and all the sulphur from the filtrate was expelled by boiling with hydrochloric acid. The resulting solution was of course free from the heavy metals, but it contained marked traces of calcium, strontium, sodium, potassium, and possibly magnesium. After two successive crystallizations from water the salt was still found to contain very small amounts of these metals, but after two precipitations by alcohol the spectroscope was unable to show any impurity in it except a trace of the ever present sodium, upon very careful testing. The two hundred grams of pure salt thus obtained were then ignited in small portions at a dull red heat. The residue was dissolved in a platinum dish and crystallized, and the crystals were dissolved in pure water. After filtration the solution was acidified by hydrochloric acid and again brought to crystallization. A portion of the salt thus formed (Sample II.a) was used for Analyses 19, 26, 30, and 36, while the remainder was again ignited in platinum, and was recrystallized twice more after filtration and very faint acidification with hydrochloric acid. The last mother liquor was evaporated to dryness in platinum, and served for Analyses 23, 27, and 37 (II.b). The purest crystals were partly dried over a steam bath, powdered in an agate mortar, and exposed to a moist atmosphere until constant in weight. These crystals (Sample II.c) served for Analyses 28, 29, 38, 39, 40, and 41. An essentially similar preparation, containing somewhat more occluded water, was used for Analyses 42 and 43.

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* See these Proceedings, XXVIII. 19.

A third sample of baric chloride was prepared from a part of the carbonate used for the preparation of baric bromide, and hydrochloric acid which had been distilled twice in platinum. This was purified in the usual fashion, and served for Analysis 24.

These preparations each gave every evidence of being pure. After most careful fractional separation of the greater part of the barium no trace of calcium or strontium could be found, even in large samples, by means of the spectroscope. The trace of sodium visible undoubtedly crept in during the fractional treatment used to prepare the specimen for spectroscopic examination, for the salt itself before the fractionation showed no more sodium than the surrounding air. The effort was made wholly to free the salt from silica by means of repeated ignition and solution, and the use of platinum vessels; but no proof can be given that it did not contain one or two parts in a hundred thousand of this impurity. The quantitative comparison of these preparations which is made further on, furnished conclusive proof of their similarity, at any rate. If the results are reduced to the basis of 100.000 parts of argentic chloride, and arranged according to the sample of baric chloride used, the following averages are obtained.*

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* From these determinations all those made according to Stas's first and second methods have been omitted, since these methods proved to be unsatisfactory. Hence Preparation I.b is not represented in the table. The high result from Sample II.a (Experiments 26 and 36 are parts of the same analysis) was due to a slight mechanical error.

		Parts of Baric Chloride corresponding to 100.000 parts of Argentic Chloride.
Preparation I.a,	Experiments 22, 25,	72.649
" I.c,	" 20, 21, 35,	72.651
" II.a,	" 26, 36,	72.668
" II.b,	" 23, 27, 37,	72.650
" II.c,	" 28, 29, 38, 39, 40, 41, 42, 43,	72.657
" III.	" 24,	72.650
	Total average,	72.654

It may be remarked that the purest specimen (Preparation II.c) gave an average result which is very close to the average of all the specimens.

Silver. — A number of different preparations of this metal, which served as one of the fundamental standards of reference, were used during the course of the work. For the final experiments pure argentic chloride remaining from earlier work was reduced by means of pure sodic hydrate and invert sugar, the invert sugar having been prepared in the first place by heating a strong solution of the purest obtainable cane sugar with a little hydrochloric acid at 100°. After a very thorough washing the metal resulting from this reduction was fused upon hard-wood charcoal in the flame of an ordinary blast lamp, and divided into two parts.

One half of this silver was purified at once by electrolysis according to the manner described in a former paper,* and was used in Analyses 30, 31, 32, 35, 36, and 37. The other half was dissolved in the purest nitric acid, and precipitated again with hydrochloric acid; then the argentic chloride was digested with aqua regia, very thoroughly washed with water, and again reduced to the metal. The last product was fused into large buttons upon sugar charcoal, and purified by electrolysis as before. The current obtained from seven or eight gravity cells is amply sufficient for the purpose. This doubly refined silver was used in Experiments 33, 34, 38, 39, 40, 41, and 43.

The silver used in Experiment 42 was prepared in the first place by Mr. H. F. Brown, according to the cuprous ammonic sulphite method of Stas.† Although the substance thus prepared gave every outward evidence of perfect purity, it was once again purified, this time by means of the electrolytic method used in the case of the previous specimens.

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* These Proceedings, XXVIII. 22.

† Untersuchungen, etc. (Aronstein), pp. 34 and 113.

The three samples of beautiful crystals of silver thus obtained by electrolysis naturally contained a minute amount of imprisoned mother liquor, which is best expelled by fusion. Many precautions were taken to prevent the absorption of an impurity during this process.

In the first trials pure hard-wood charcoal was used to support the metal during its fusion in the flame of the ordinary blast lamp (Experiments 30, 31, and 32). Afterwards a cupel of sugar charcoal was substituted for the wood charcoal. Such cupels are readily made by mixing finely powdered pure sugar charcoal with about a third of its weight of pure powdered sugar, and igniting in closed moulds. The silver used in Analyses 35, 36, 38, 42, and 43 was fused in this way.

A possible absorption of sulphur from illuminating gas being feared, a number of buttons of silver were fused upon the sugar charcoal cupels by the use of a blast lamp in which only pure alcohol, vaporized in a steam bath, was burnt. Such silver was used in Experiments 33, 34, 37, 39, and 40. All of these specimens of silver had been cooled with care in the centre of a strongly reducing flame, to prevent the absorption of oxygen; and any button which showed a trace of such absorption was of course discarded. Proof has already been given * that no oxygen is held after such treatment; but in order to "make assurance doubly sure" three grams and a half of the purest crystals were placed upon a boat made of sugar charcoal, enclosed in a stout porcelain tube, and fused in a vacuum (Experiment 41).

The results obtained from these different varieties of silver may well be recorded here, although the details must be reserved until nearly the end of the present paper. The first specimen of silver fused upon wood charcoal was used in experiments which were vitiated by other serious errors, so that the results from it need not be given. The figures given below represent the amount of silver required exactly to precipitate 100.000 parts of baric chloride.†

(1.)	First specimen,	sugar charcoal,	illuminating gas,		103.600
(2.)	"	"	"	alcohol,	103.604
(3.)	Second	"	"	illuminating gas,	103.600
(4.)	"	"	"	alcohol,	103.599
(5.)	"	"	"	fused in vacuum,	103.599
(6.)	Third	"	"	illuminating gas,	103.600
			Average,		103.600

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* These Proceedings, XXV. 198.

† The results obtained from Stas's second method, described later, are omitted from this series.

Of these figures (2), (5), and (6) represent single results, and the other figures represent averages. Since a number of samples of baric chloride and a number of different methods of comparison were used in the individual cases, the averages, which to some extent eliminate the differences, are more reliable than the single results. It is evident that the different varieties of silver were quite as nearly alike as the accuracy of our present processes demands.

The investigation of the silver closed with a direct determination of the amount of sulphur present in a sample which was purposely made under conditions as favorable as possible for the retention of this impurity. Twelve grams of silver, which had been prepared by the sulphite method and fused three times successively for a long period in the flame of an ordinary blast lamp, were dissolved and precipitated by electrolysis in a solution of silver nitrate prepared from the same silver. The residual electrolyte, which must have contained all the sulphur, was much diluted, freed from silver by the addition of hydrochloric acid, and evaporated on the steam bath to free it from nitric acid. This solution yielded 1.4 milligrams of baric sulphate, corresponding to 0.2 milligram of sulphur. Hence under these conditions the silver held only $\frac{1}{60,000}$ of its weight of sulphur; and it is fair to conclude that according to the usual method of subjecting the silver only to a single brief fusion not more than $\frac{1}{200,000}$ of its weight would be absorbed. This result is in entire accordance with the quantitative and qualitative results already described; it shows that silver fused once in illuminating gas may be used without appreciable error for all ordinary work.

The preparation of pure water, alcohol, sulphuric and nitric acids, and all other necessary materials, has been discussed in previous papers.*

Standard Solutions. — Several standard solutions were so constantly used during the research that they may well be described at the beginning. In the first place, exactly a gram of silver was dissolved in a slight excess of nitric acid, with the usual precautions,† and diluted exactly to a litre. A solution of pure hydrochloric acid was then made of equivalent strength by comparison with pure sodic carbonate, and verified by comparison with the silver solution. This last comparison is not easily made, for the argentic chloride separates but slowly from a solution so dilute. It was found most convenient to add a very slight excess of silver, to warm, agitate, and filter the solution, and to determine the excess in the filtrate by means of an equivalent solution of ammonic sulpho-cyanate, after the method of Volhard. Sanger[*] has pointed out that the solubility of argentic chloride seriously affects the accuracy of this method unless the argentic chloride is filtered off before the addition of the sulpho-cyanate; and the experience of this Laboratory had independently led to the same conclusion. It is to be hoped that Clemens Winkler observed this precaution in his interesting analyses of cobaltous and nickellous chloride;[†] if not, the atomic weights obtained are probably too high.

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* These Proceedings, XXVI. 245-249; XXVIII. 23.

† Ibid., XXV. 198; XXVIII. 24.

The three equivalent solutions of argentic nitrate, hydrochloric acid, and ammonic sulphocyanate each corresponded exactly to a milligram of silver for each cubic centimeter. These solutions are referred to whenever a standard solution is mentioned below.

It is needless to say that the measuring apparatus was all calibrated with great care; moreover, for the final experiments the solutions were weighed in small flasks provided with tightly fitting graduated pipettes, as well as measured. This last precaution was hardly necessary, however. Of course, the ordinary methods of volumetric analysis are not applicable to the determination of atomic weights; but when the greater part of a reagent has been weighed out, the last few milligrams may be added by the measurement of a very dilute solution with an accuracy quite equal to that obtainable upon a balance.[‡]

RATIO OF BARIC CHLORIDE TO BARIC SULPHATE.

It is well known that such a ratio as that of baric chloride to baric sulphate could form at best but a very poor basis for determining the atomic weight of barium.[§] An experimental error in the process is necessarily magnified many times when referred to the constant sought. Nevertheless, since five distinguished chemists have tried this method, it was thought expedient to attempt it, in order to show if possible the cause of the great discrepancies in their results.

The investigation of the ratio occupied several months, but the report of it will be greatly abbreviated. The principal cause of error was found in the very decided occlusion of baric chloride by baric sulphate, a fact which has already been discussed in a previous paper.* This cause of error was never wholly avoided, although by repeated treatment of the baric sulphate with sulphuric acid, all but a few tenths of a milligram of chlorine were found to be expelled. Whether or not the baric chloride is occluded in the form of a so called "solid solution," as E. A. Schneider suggests in a recent paper with regard to the occlusion of ferric sulphate by baric sulphate,† the fact remains that an appreciable amount of baric chloride is very firmly held. Possibly nothing short of the true solution of all the baric sulphate in sulphuric acid could drive off all the chlorine; and such treatment would be likely to introduce errors as large as the one which it would obviate.

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[*] These Proceedings, XXVI. 34.

[†] Zeitschr. Anorg. Chem., IV. 10.

[‡] This point, among others, seems to have been misunderstood by G. Hinrichs, of the College of Pharmacy, St. Louis. (Chem. News, LXVIII. 171.)

[§] Ostwald, Allgemeine Chemie, I. 23. These Proceedings, XXVIII. 11.

Besides this inclusion of baric chloride, which tends to raise the apparent atomic weight of barium, another circumstance, the solubility of baric sulphate in water, may work in the same direction. This second cause of error was quite eliminated in the present work. A third cause of error with an opposite tendency exists; namely, the obstinacy with which baric sulphate retains the last traces of the excess of sulphuric acid and water used to precipitate it. It must be borne in mind that the retention of 0.2 milligram of either substance counterbalances numerically the retention of nearly two milligrams of baric chloride.

Two series of determinations were made, one by the direct addition of pure sulphuric acid to a concentrated solution of pure baric chloride in a platinum crucible, the other by precipitation in dilute solution after the usual fashion. In the latter case the baric sulphate in the filtrates, usually amounting to about a milligram and a half, was determined by evaporation in large platinum dishes. In each series every specimen of baric sulphate was of course heated with successive drops of pure sulphuric acid at a dull red heat until the weight became constant. Eight experiments which were not complicated with mechanical errors are recorded in the note-book. The two series gave the same result, a hundred parts of baric chloride yielding 112.073 parts of baric sulphate. The highest result was 112.087, and the lowest 112.060. Berzelius found 112.175, Turner 112.19, Thomson about 112.15, Struve 112.094, and Marignac 112.011.

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* These Proceedings, XXVI. 258.

† Zeitschr. für Physikal. Chem. (1892), X. 425.

Owing to the chemical errors which have just been pointed out, the results given above are of no real value. For this reason the individual data are omitted. The uncertainty of the result 112.073 is probably as much as a unit in the second decimal place; therefore the atomic weight of barium computed from it, 137.43, cannot be relied upon to within 0.2. The different errors tend to eliminate one another, so that the result is by chance near the true one.

SOLUBILITY OF ARGENTIC CHLORIDE.

Since it is evident that no satisfactory results are to be obtained from the ratio just discussed, the careful investigation of the ratios of silver and argentic chloride to baric chloride assumes even greater importance than before.

The solubility of argentic chloride is the most serious difficulty which is to be overcome in this investigation. Gay Lussac knew that the filtered liquid which remains after mixing equivalent amounts of solutions of argentic nitrate and a chloride invariably gives a precipitate with an excess of either reagent, showing that some argentic chloride must remain in solution. Mulder, in 1857,* recognized very clearly the same fact, and pointed out, with the help of a great number of detailed experiments, just what influence this fact has upon the titration of silver by Gay Lussac's method.

Mulder wrongly ascribed the solubility of argentic chloride to the presence of the alkaline nitrate resulting from the decomposition, for he believed that the curdy precipitate was wholly insoluble in pure water, or in water acidified with a reasonable amount of nitric acid. Six or eight years later Stas,† without knowing of Mulder's work, clearly recognized the difficulty, but fell into serious blunders in interpreting it. Before 1872, however, when his noted researches on the "chemical statics" of argentic chloride and bromide began to appear,‡ he had become familiar with Mulder's work, and had adopted many of his points of view.

In these last reseaches Stas found that freshly precipitated voluminous argentic chloride was soluble to a very large extent (over ten milligrams to a litre) in the purest water, and that nitric acid or the alkaline nitrates had no appreciable effect upon the solubility. The pulverulent precipitate obtained by continual shaking he found to be much less soluble, only 0.7 milligram being dissolved by a litre of pure water. Nitric acid increases to a sensible degree this last quantity, the increase being approximately proportional to the amount of acid present.

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* Mulder, "Essayeer-Methode van het Zilver," Scheikundige Verhandelingen en Onderzoekingen, 1 Deel, 1 Stuk, 1857. Translated by Grimm, "Die Silberprobirmethode," Leipzig, 1859.

† "Untersuchungen," etc., translated by Aronstein (Leipzig, 1867), pp. 46, 56, 59, and 295

‡ Annales de Chim. et de Phys., 4th series, XXV. 22; and 5th series, III. 145 and 289.

Mulder knew well that it was possible wholly to precipitate either silver or chlorine by the addition of a sufficient amount of the other reagent, but wrongly assumed that the amount of the reagent required was a direct measure of the solubility of argentic chloride. This misconception probably arose from a theoretical discussion of very doubtful value; its effect was to make Mulder's estimate of the solubility rather excessive. Stas recognized the fact for the first time, that much more silver is required to precipitate the chlorine in solution as silver chloride than is enough directly to combine with it. A very tedious series of experiments led him to the conclusion that for every molecule of argentic chloride dissolved just three molecules of argentic nitrate or of a chloride were required to complete the precipitation. In 1881 Cooke called attention to some of the same facts.*

Much time has been spent during the present research upon the subject, for its importance with regard to the analysis of baric chloride was very evident. The experiments were largely a repetition of Stas's, with occasional variations suggested by the case in hand. Mulder and Stas having wholly done away with the old idea of the insignificance of the action of light on the haloid compounds of silver, the greatest care was taken with regard to the protection of the precipitates from diffused light. Work with them was performed wholly in a dark room lighted by means of illuminating gas shining through thick orange glass; and even here the flasks were always covered by two or three thicknesses of black cloth when left to themselves.

In determining the solubility of argentic chloride a number of experiments were made, first by colorimetric and "opalimetric" methods. The coloration produced by hydric sulphide and the opalescence produced by hydrochloric acid were compared with similar phenomena produced by known amounts of silver. Very much experience is needed to obtain satisfactory results with either of these methods, so that a more direct method of determination was sought.

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* These Proceedings, XVII. 7. Cooke also studied the action of hot water upon argentic chloride.

An opalescent solution produced by the addition of hydrochloric acid or argentic nitrate to a solution of argentic chloride often requires many weeks to deposit its suspended salt, even when warmed and shaken, if the flask is kept wholly in the dark. The effort to evaporate the solution by boiling in vessels partially closed to exclude the dust, proved equally unsatisfactory. Hence in order to weigh very small amounts of dissolved argentic chloride it was necessary to evaporate the solutions upon the steam bath in suitably protected glass dishes. In order to determine the magnitude of any possible errors which might arise from this method of treatment a number of check experiments were made. In the first place dilute solutions of argentic nitrate were evaporated to small bulk with the addition of nitric acid. The evaporated solution was filtered through a small paper, and the ash of the washed filter was dissolved in nitric acid and titrated with a weak standard solution of ammonic sulphocyanate,* after the method of Volhard. Three experiments showed that an amount of silver equal to about 0.02, 0.01, and 0.00 milligram respectively had been retained by the filter. These experiments proved that the precautions taken to prevent dust or foreign materials from reaching the surface of the solutions during the process of evaporation had been sufficient for their purpose; also, that no very important amount of silver was held by the paper.

Having determined these facts, the next step was to determine whether all of a very small known amount of argentic chloride could be recovered. A few preliminary experiments showed that in order to reduce and recover all of the silver by the ignition of the filter paper it was necessary to keep the precipitate in a finely divided state. This end is easily accomplished by using a solution dilute enough to prevent the clotting of the opalescent chloride. Thus one cubic centimeter of the weak standard hydrochloric acid precipitated enough argentic chloride from a slight excess of the nitrate to require after reduction by the burning of the filter 0.97 and 0.99 cubic centimeter of the sulphocyanate solution. Although the evaporation was conducted in dull diffused light, the argentic chloride was not discolored.† These experiments showed that a small amount of argentic chloride could be nearly all recovered from a small volume of solution.

The next experiments were made with large volumes of solutions containing about 0.2 gram of silver, a very little baric nitrate, and a small amount of nitric acid, besides the measured amount of standard hydrochloric acid. Two experiments, after filtration, ignition, and titration as before, indicated that 1.01 and 1.02 milligrams of silver were precipitated by one cubic centimeter of hydrochloric acid, instead of just one milligram. Again, with all the other conditions just the same, 0.50 c.c. of hydrochloric acid precipitated in two cases 0.62 and 0.59 milligram of silver. In order to determine whether the presence of large amounts of baric nitrate might make any essential difference, these experiments were repeated with the addition of five grams of the purest preparation of this salt,* quite free from chlorine. In this way 0.50 c.c. of hydrochloric acid yielded 0.57 milligram of silver and 0.20 c.c. precipitated 0.27 milligram of silver. The last six experiments showed that the presence of a considerable excess of silver in solution causes the precipitation of a slight excess of silver with the chloride.

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* See page 66 of this paper.

† Compare Pohl, Jahresbericht 1851, p. 369. Quoted by Mulder, Silberprobirmethode, p. 19.

Two experiments with neutral solutions treated in the same way showed much more marked gains; one exposed to the air during evaporation for eight hours gained 0.13 milligram of silver; and the other, evaporated for twenty-four hours, the water being replaced from time to time, gained 0.32 milligram. These gains might have been due to the action of organic matter in the absence of nitric acid, or the action of alkali dissolved from the glass; in any case, the necessity of the presence of free acid was shown.

In the work which follows it was several times necessary to evaporate strongly acid solutions of argentic chloride containing only a very slight excess of silver, hence parallel determinations under these conditions were very essential. In this way three successive experiments yielded respectively 0.38, 0.38, and 0.37 milligram of silver, instead of 0.50 milligram, which should have been obtained; one experiment gave 0.52 instead of 0.60, and two more gave respectively 0.90 and 0.93, instead of 1.00. Hence, when much nitric acid and very little silver are present, the amount of metal found is too small instead of too great.

These determinations all together show that the evaporation of solutions of argentic chloride upon the water bath is a process carrying with it small errors, some plus and some minus, which are reasonably constant under constant conditions. They show also that the presence of baric nitrate does not in the least alter the accuracy of the determination, which depends chiefly upon the relative amounts of argentic nitrate and nitric acid present in each case. They moreover furnish a means of correcting results obtained by the method in hand. A solution containing two tenths of a gram of argentic nitrate, three grams of nitric acid, and a very small known amount of argentic chloride, evaporated for four or five hours, yields about 0.00006 gram too much silver, and a similar solution containing only a few milligrams of argentic nitrate yields about 0.0001 gram too little. The bearing of these facts upon the subject will presently be made more evident.

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* These Proceedings, XXVIII. 16, 19.

It was now possible to determine the solubility of argentic chloride less crudely. Half a litre of the purest water, after being shaken occasionally with the purest argentic chloride for two hours, yielded 0.50 milligram of silver, and a similar preparation, which had been allowed to stand for twenty-four hours with more frequent shaking, yielded 0.60 milligram. The solubility of this argentic chloride is thus found to be about 1.5 milligrams per litre. The result is not far from the mean of the colorimetric tests.*

To determine the influence of nitric acid upon the solubility, four grams of this substance were added to over a litre of pure water, and the mixture was shaken with the same argentic chloride. 300 cubic centimeters of the solution yielded 0.47 milligram of silver, and two portions of 400 cubic centimeters each yield 0.56 and 0.57 milligram of silver respectively. After adding the appropriate correction, and taking the mean of these determinations, the solubility is found to be about 2.3 milligrams per litre.

In a number of analyses exactly equivalent amounts of baric chloride and argentic nitrate in dilute solution were shaken together, and both chlorine and silver were determined in the filtrate. These analyses were primarily to determine the atomic weight of barium, and will be described later; but since the chlorine was found to be present in the filtrate in amounts almost exactly equivalent to the silver, they may be used also to measure the solubility of argentic chloride in solutions containing about 2.5 cubic centimeters of nitric acid, and 3 to 8 grams of baric nitrate. In one case, where the solution had been shaken with the argentic chloride for ten days, the solubility was found to be about 1.6 milligrams per litre; in another, violently shaken, but allowed to stand for a shorter time, it was found to be about 1.7

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* It is noteworthy that Kohlrausch and Rose have found the solubility of argentic chloride to be 1.52 milligrams per litre at 18°. This determination was based upon the electrical conductivity of the solution. (Zeit. Physikal. Chem., XII. 234.)

milligrams per litre; and in a third, much less violently shaken, but allowed to stand for a week, it was as much as 2.7 milligrams per litre. In each of these cases the temperature was about 20°.

These results are, as one would expect, between the limits set by Stas; for the precipitate was in the state usually observed, having lost its first flocculence, and not having been wholly converted into powder.

A careful series of experiments was made to confirm Stas's statement that the chloride is absolutely insoluble in water containing an excess of argentic nitrate. It is not needful further to describe these experiments, except to state that the confirmation was wholly satisfactory. In the course of this work I was able to detect repeatedly one part of chlorine in thirty million parts of water, by careful comparison in strong sunlight after treatment with excess of argentic nitrate. The very faint opalescence of course very soon disappears, owing to the blackening of argentic chloride by the powerful light.

RATIO OF THE CHLORIDES OF SILVER AND BARIUM.

The properties of the two chlorides having been studied as far as they are concerned in the present work, it was now possible to compare their molecular weights. Very definite advice with regard to the precautions necessary in such a comparison has been given by Stas,* and most of his suggestions have been found of use. One recommendation, however, although most useful for ordinary work, is of questionable propriety when applied to the most precise work: In order to prevent argentic chloride from being dissolved by the water used for washing it, Stas advises the exclusive use of a very dilute solution of argentic nitrate for the purpose.† I have found it very difficult wholly to free argentic chloride from traces of the nitrate, even by long continued shaking with pure water, and of course this difficulty is increased by the presence of additional impurity. The small amount of argentic nitrate which is certain to be left behind, according to the method of Stas, decomposes and blackens a little of the chloride upon fusion, even in the dark; and no suitable correction can be applied to counteract the error. Accordingly, pure water was always used for the final washings during the present work.

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* Mém. de l'Acad. Belg., Vol. XLIII. Part II. p. 66.

† Professor Cooke also suggested this method of procedure. (These Proceedings, XVII. 7.)

These wash waters were all evaporated, and the small amount of argentic chloride present was determined in the manner which has already been described. It is thus tolerably certain that the necessary errors of the analytical process did not exceed the tenth of a milligram.

In two preliminary experiments very pure baric chloride was ignited at a dull red heat to constant weight, dissolved in water, and corrected for the amount of alkali found. It was then precipitated, when perfectly cool, by pouring it into a slight excess of silver dissolved in nitric acid, and diluted with about forty times its weight of cold water. The precipitate was very thoroughly shaken for several days, and washed by decantation until the wash water was no longer acid. It was then transferred with great care to a Gooch perforated crucible, washed for some time longer, dried at 180°, and weighed. Both of the precipitates were slightly colored, and each lost about $\frac{1}{10000}$ of its weight upon fusion in a covered porcelain crucible. In calculating the results it was necessary to subtract the amount of argentic chloride equivalent to the small *excess* of hydrochloric acid usually added in determining the amount of alkali formed by the ignition, as well as to add the amount of argentic chloride found in the wash water. The corrected results are given below, the details having been omitted; but the particulars will be given with regard to all the important determinations.

PRELIMINARY DETERMINATIONS.

$2\,AgCl : BaCl_2$.

No. of Exp.	Corrected Weight of Baric Chloride.	Corrected Weight of Fused Argentic Chloride.	100,000 parts of Argentic Chloride correspond to *n* parts Baric Chloride.	Atomic Weight of Barium.
	Grams in Vacuum.	Grams in Vacuum.	$n =$	
18	6.7295	9.2637	72.644	137.411
19	5.4597	7.5161	72.640	137.400
	Average,	....	....	137.406

Since the experiments were carried on in the dark, the purplish color of the fused argentic chloride indicated that argentic nitrate had been occluded, in spite of the considerable care used in washing the precipitate. In order to determine whether this occlusion had been due to the concentration of the silver solution, an experiment was made by pouring a solution of a definite amount of pure baric chloride into a very strong solution of argentic nitrate. 2.6088 grams (corrected) of baric chloride yielded 3.5929 grams (corrected) of carefully washed argentic chloride. The ratio deduced from these figures is $2\ AgCl : BaCl_2 = 100 : 72.609$, a result almost $\frac{1}{2000}$ lower than the last; and the consequent value of the atomic weight of barium is only 137.31. The argentic chloride was of a very deep purple color.

The outcome of these experiments showed the necessity of Stas's usual practice of having the silver solution very dilute; in the subsequent work the dilution was usually 1 : 100, and sometimes even greater.* Moreover, the nitrate was always in future poured gradually into the baric chloride, so that until the very last an excess of chlorine should be present in the solution.

In the first series of the final group of experiments the baric chloride was ignited at a dull red heat in air or nitrogen; in the second series the salt was ignited and fused at a bright red heat in a stream of pure hydrochloric acid; and in the third it was not ignited at all. The simplest manner of explaining the method of procedure adopted in the three series of analyses which follow is to give the detail of one of the experiments.

Experiment 20. Very pure baric chloride, which had been prepared by many successive precipitations from aqueous solution by hydrochloric acid and alcohol (Sample I.c), was coarsely powdered and gradually heated to bright redness by means of a Berzelius spirit lamp in a double platinum crucible. In order to prevent as much as possible the decomposition of the salt, the long continued ignition was conducted in a stream of pure nitrogen. A large part of the salt was fused during the process. After having been cooled for eight hours over phosphoric oxide in a desiccator, the tightly covered inner crucible was rapidly weighed, and the weight of baric chloride was found to be 6.36793 grams in the air. Since the atmospheric pressure and temperature at the time of weighing were respectively 76 c.m. and 20°, the salt would have weighed 6.36900 grams in a vacuum. The solution of the baric chloride in pure boiled water in a large platinum dish was perfectly clear, and the crucible itself was found to have lost only 0.02 milligram in weight. The clear liquid upon being titrated at once with standard hydrochloric acid* was found to require 3.40 cubic centimeters of the solution in order to remove the color of the trace of phenol phthaleïn added, and 0.64 cubic centimeter more to reach the point at which methyl orange began to show an excess of acid. An excess of yet 0.26 cubic centimeter was added in order to be certain of the end-point. According to page 57, the correction to be added to the weight of the baric chloride corresponding to the first addition of acid was 0.71 milligram, while the correction corresponding to the second addition was 0.03 milligram. Hence, the true weight of the baric chloride in vacuum, if none had been decomposed by heat, would have been 6.36974.

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* In some cases Stas used only fifteen to thirty cubic centimeters of water for every gram of silver, in spite of his good advice to the contrary. Mém. Belg., etc., XLIII. Part II. p. 11.

The solution was transferred with the greatest care to a glass stoppered Erlenmeyer flask, and diluted to about one hundred and fifty cubic centimeters with cold water. To it was then gradually added in the dark room the cold solution of about 6.72 grams of silver (about $\frac{1}{50}$ excess). The metal had been dissolved in thirteen cubic centimeters of the purest nitric acid, the lower oxides of nitrogen had been expelled, and the whole had been diluted to over six hundred cubic centimeters.

The precipitate was shaken occasionally with the liquid for several days in perfect darkness; and the filtrate, which could contain no trace of chlorine, was separated by means of the indispensable Gooch crucible. After having been passed several times through the crucible, in order to avoid the loss of any shreds of asbestos, the filtrate was set aside. The precipitate was violently agitated with renewed portions of cold water until the wash water was absolutely neutral, and was then transferred to the crucible by means of a jet of water. The last particles of argentic chloride were removed by shaking the stoppered flask violently with a little water. Subsequent testing with ammonia and nitric acid showed that no argentic chloride remained in the flask. The thirteen hundred cubic centimeters of wash water were evaporated, and the small amount of resulting argentic chloride was collected upon a small washed filter of the best quality. After the rapid ignition of the filter paper in a porcelain dish, the ash was found to contain 0.70 milligram of silver, according to Volhard's method. Hence, 0.93 milligram of argentic chloride had been dissolved. The main mass of the precipitate was dried at 180°; and after having been carefully weighed it was transferred to a porcelain crucible, weighed again, fused in an air bath, and weighed yet again. It is needless to say that organic matter was carefully excluded during all the operations, but nevertheless the argentic chloride was not absolutely colorless after fusion. Perhaps the trace of phenol phthaleïn and methyl orange may have caused a slight decomposition. It will be seen how the introduction of these indicators was avoided before the close of the investigation.

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* See page 66 of this paper.

The final corrected weight of the argentic chloride was found as follows: —

		Grams.
Weight in air of AgCl in Gooch crucible	=	8.76657
Correction to vacuum (T° = 22°, H = 76 c.m.)	=	+0.00062
Weight in vacuum of AgCl in Gooch crucible	=	8.76719
Loss on fusion in porcelain crucible	=	−0.00050
Weight of main mass of fused AgCl	=	8.76669
Weight of AgCl found in wash water	=	+0.00093
Total argentic chloride	=	8.76762
Corresponding to 0.26 c.c. standard HCl added in titration	=	−0.00035
Corrected weight of argentic chloride in vacuum	=	8.76727

Since it seemed hardly probable that either of the chlorides was in this case weighed more accurately than within 0.1 milligram, the fifth place of decimals is omitted below. This practice was always adhered to unless the fifth place seemed to have some significance.

Experiment 20 then leads us to conclude that the ratio of argentic chloride to baric chloride is 8.7673 : 6.3697 = 100.000 : 72.653. Hence, the atomic weight of barium is easily found to be 137.435, a result which agrees almost exactly with that obtained from baric bromide.

The other analyses were conducted in a similar manner. In some cases, where it was suspected that the wash water carried with it a trace of finely divided asbestos, the whole quantity was filtered through a washed filter, and the weight found, if appreciable at all, was added to the weight of the Gooch crucible. The table given below is probably comprehensible without further remark, except perhaps the statement that the two figures given in the third column represent the corrections for the baric hydroxide and baric carbonate respectively.

The weights in the following cases are reduced to the vacuum standard.

RATIO OF ARGENTIC AND BARIC CHLORIDES.

FIRST SERIES.

No. of Exp.	Baric Chloride weighed.	Alk. cor. See p. 57.*	$BaCl_2$ corrected for Alkali found.	Argentic Chloride found (Fused).	AgCl corresp. to extra HCl.	AgCl in Wash Water.	Total Argentic Chloride.	Ratio 2 AgCl : $BaCl_2 = 100 : x$.	Atomic Weight of Barium.
	grams.	c c.	grams.	grams.	m. gr.	m. gr.	grams.		
20	6.3690	3.4 0.6	6.3697	8.7667	0.35	0.93	8.7673	72.653	137.435
21	3.7764	0.3 0.2	3.7765	5.1973	0.20	0.80	5.1979	72.654	137.440
22	3.5846	0.0 0.7	3.5846	4.9332	0.13	1.10	4.9342	72.648	137.423
23	1.5084	0.3 0.3	1.5085	2.0759	0.24	0.86	2.0765	72.646	137.417
24	3.2160	1.1 0.9	3.2163	4.4254	0.64	2.32	4.4271	72.650	137.429
							Average	72.649	137.428

The second series of determinations is distinguished from the first by the fact that the baric chloride was fused in an atmosphere of pure dry hydrochloric acid, being contained in a platinum crucible provided with a perforated cover. No phenol phthaleïn was added to the salt after its solution, and only a trace of methyl orange, in order to prove its absolute neutrality. Hence, the danger of a slight reduction of silver by compounds of carbon was much lessened. In all other respects the analysis was conducted in a manner similar to that employed in the last series, except that even greater care was used.

RATIO OF ARGENTIC AND BARIC CHLORIDES.

SECOND SERIES.

No. of Exp.	Weight of Fused Baric Chloride.	Weight of Fused Argentic Chloride.	AgCl corresp. to extra HCl.	AgCl in Wash Water.	Total Argentic Chloride.	Ratio 2 AgCl : $BaCl_2 = 100 : x$.	Atomic Weight of Barium.
	grams.	grams.	m.gr.	m.gr.	grams.		
25	1.52384	2.09730	0.00	0.20	2.09750	72.650	137.429
26	5.36010	7.37590	0.10	0.30	7.37610	72.669	137.481
27	3.92244	5.39771	0.12	1.47	5.39906	72.650	137.429
					Average	72.6563	137.446

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* Compare also these Proceedings, XXVIII. 12, also 26.

The third series differed from the two others in that the baric chloride was not ignited at all. In the two analyses thus made, the true weight of the anhydrous baric chloride taken in each case was calculated from the weight of the homogeneous powdered crystallized salt actually weighed. The determinations of the water of crystallization given on page 61, which were made at this time, upon this identical sample, showed with great certainty that the percentage of anhydrous salt present must have been 85.2282. Of course, no indicator of any kind was added to the solution before the precipitation. The argentic chloride after having been fused and cooled was of a most beautiful pearly lustre, without a trace of grayness; and in every respect the analyses appeared to be satisfactory.

RATIO OF ARGENTIC AND BARIC CHLORIDES.

Third Series.

No. of Exp.	Weight of Crystallized Baric Chloride.	Calculated Weight of Anhydrous $BaCl_2$.	Weight of Fused AgCl.	AgCl in Wash Water.*	Total Argentic Chloride.	Ratio $2\,AgCl : BaCl_2 = 100 : x$.	Atomic Weight of Barium.
	grams.	grams.	grams.	milligrams.	grams.		
28	7.00617	5.97123	8.21488	4.0	8.2189	72.6524	137.435
29	3.85330	3.28410	4.51770	2.2	4.5199	72.6587	137.453
					Average	72.6555	137.444

The discussion of all these results will be found under a later head.

Ratio of Metallic Silver to Baric Chloride.

In determining this ratio the solubility of argentic chloride plays a much more damaging part than in the determination of the previous one. The uncertainty may easily become as great as thirty or forty milligrams in the weight of the silver, — an amount so enormous as to render accurate determination apparently impossible. Aside from this uncertainty, due to the existence of the two end-points, the observation of the point at which a drop of one solution or the other absolutely ceases to produce a precipitate is a very trying matter. The physical condition of the observer, and his practice in observation of this sort, have much to do with his determination of the presence or absence of a faint cloud at the top of the vessel under observation. The phenomenon is one which gradually fades away as more and more silver or hydrochloric acid is added, the last opalescence appearing only after some time. Often when no cloud is visible at the end of an hour, a very evident one is to be seen in two hours. The amount of light at hand is also an important factor in the determination. Temperature produces a very important effect on the solubility of argentic chloride; and this effect is tripled when it is referred to the solution which is being added. The results are thus far less satisfactory than similar results obtained with the bromide.

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* Since the excess of silver was very slight, and a portion of the argentic chloride in the filtrate was determined by the evaporation of the strongly acid solution of baric nitrate, it was necessary to apply the correction of +0.0001 gram, described on pages 72 and 73, to the amount of argentic chloride found in the wash water. The values given above have been thus corrected.

For preliminary experiments the method used by Stas in his early analyses * was adopted. The method consisted in the addition of an excess of silver to the solution of baric chloride, a standard solution of hydrochloric acid being used to determine this excess. At first the atomic weight thus obtained corresponded very closely to that obtained by the last ratio, but as the work proceeded the apparent atomic weight of barium steadily rose. The reason for this anomaly was not clear for a long time; but in the end it was evident that the apparent accuracy of the first results had been due to the mutual elimination of two opposite errors. The occlusion of argentic nitrate by argentic chloride tended to require too much silver, and the method of titration required almost equally too much hydrochloric acid. When more care was taken with regard to the dilution of the argentic nitrate, and as the observer became more and more practised in the delicate observation of the end point, the first error steadily decreased, and the second steadily increased. Hence, they no longer counterbalanced one another. A long time was spent in finding that this first method, used by Stas in his early analyses of lithium, sodium, potassium, and ammonium chlorides, was quite false. Even relative results by this method, such as Stas's comparison of the different varieties of silver, can have no important value, because it is wellnigh impossible to make all the conditions absolutely constant. It is almost needless to say that these remarks apply only to this early method, and not to Stas's later work. Naturally he made errors at first. It is much to be regretted, however, that he did not point out more clearly after-

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* "Untersuchungen," etc. Leipzig, 1867.

wards the serious nature of these errors, which he clearly appreciated. Most of the investigations of Stas remain models of precision; and no one who has not attempted practically to follow in his footsteps can form an adequate idea of the greatness of his success.

Stas's study of the "Statics of Argentic Chloride" has been already referred to. As a result of this long and valuable series of experiments, he concluded that the true end-point must be half way between the two end-points obtained by titrating in opposite directions. When this true end-point had been reached, he found that the supernatant liquid was rendered equally opalescent by equivalent amounts of hydrochloric acid and argentic nitrate. These conclusions suggested two possible methods for the solution of the problem before us; and it is worthy of remark that at least one of these methods had been suggested by Mulder fifteen years before Stas's publication.*

The unsatisfactory results obtained by the old method inclined one to subject the newer methods also to a careful testing before going further; accordingly a long series of experiments, not unlike those described by Stas, were instituted to prove them. In the first place, pure thoroughly washed argentic chloride which had been made and kept in darkness was shaken with a dilute solution of pure baric nitrate and nitric acid; and then the two end-points were determined by adding first hydrochloric acid, and afterward argentic nitrate, until no more cloudiness could be observed in either case. The results were not very satisfactory, for a reason which appeared later. Nevertheless, many experiments were made in this way, showing that the observation of Stas was at least approximately true. The observation with regard to the equality of opalescence could not be confirmed at once, because the method requires much practice; but in the end the confirmation of it was much more satisfactory than the previous one. It was clear, however, that both methods depended upon a question of judgment rather than upon definite weighing or measuring.

In default of a more satisfactory method a series of experiments upon the atomic weight of barium was made by determining both end-points and taking the mean as the true one, according to Stas's second method. During this series a curious fact became manifest. As the alternate addition of hydrochloric acid and silver nitrate proceeded, the necessary amount of each solution increased to an enormous degree. For instance, in Experiment 33 below, the first difference between the end-points was 16 milligrams of silver, while the third was as much as 34 milligrams. This change was probably due to the fact that the argentic chloride produced by the successive additions of the solutions was of the more soluble flaky variety, while the greater part of the precipitate had been so thoroughly shaken before as to become much less soluble. A larger amount of the salt in solution naturally required more of each reagent to precipitate it. This phenomenon was the chief cause of uncertainty in the attempt to confirm Stas's results. Probably the reason for his overlooking it lay in the fact that he rarely titrated backward and forward many times with the same solution.

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* Silberprobirmethode, p. 94.

In the experiments tabulated below, the baric chloride was ignited in the air, and the small amount of chlorine lost was allowed for as usual. The calculated and carefully weighed amount of pure silver was dissolved in nearly three times its weight of the purest nitric acid in a Bohemian flask provided with bulb tubes for arresting the spray. The bulbs were washed out into the flask, the nitrous fumes were expelled by heating upon the steam bath for a long time, the contents of the flask were diluted and cooled, and the argentic nitrate was added to the baric chloride in a glass-stoppered flask.

In every case the first readings of the end-points are recorded in the table as being the most trustworthy, although in some cases as much as three weeks were spent upon a single determination in titrating backward and forward. The weights are, as usual, reduced to the vacuum standard.

RATIO OF SILVER TO BARIC CHLORIDE.

First Series: Stas's Second Method.

No. of Experiment.	Corrected Weight of Anhydrous Baric Chloride.	Mean Amount of Silver required.	Difference between Extreme Amounts of Ag.	Ratio 2 Ag : $BaCl_2$ = 100 : x.	Atomic Weight of Barium.
	grams.	grams.	grams.		
30	5.9717	6.1872	0.0032	96.517	137.431
31	5.4597	5.6580	0.0140	96.495	137.383
32	3.4728	3.5988	0.0050	96.499	137.389
33	9.0726	9.4010	0.0160	96.507	137.408
34	0.6950	0.7199	0.0029	96.541	137.482
				96.511	137.419

The objections to this method have been stated already; accuracy with it is a question of judgment and keenness of sight upon the part of the observer, and absolutely constant conditions of temperature, illumination, and agitation on the part of the substance in the flask. Although great pains were taken to have these conditions as constant as possible, it cannot be claimed that they were absolutely so. Moreover, the method is so hopelessly tedious that it was finally abandoned.

In the search for a new method, the following scheme was devised. A slight excess of one or two decigrams of silver over and above the amount required to precipitate a weighed quantity of baric chloride was weighed out with the greatest care. This was dissolved and added to the baric chloride as before. The mother liquor, containing argentic nitrate, baric nitrate, and nitric acid, *but no trace of chlorine,* was filtered off with the greatest care through asbestos, and the precipitate was thoroughly shaken and washed with pure water. The wash waters were collected separately and evaporated on the steam bath in a suitably covered dish to small bulk. The trace of argentic chloride thus precipitated from them was filtered off and washed upon a very small filter, and the few milligrams of argentic nitrate in the filtrate were added to the original mother liquor. From this mixture of liquids all the silver was precipitated and weighed as argentic bromide.* The excess of silver originally weighed out is thus very simply calculated from the weight of the argentic bromide without involving a personal equation of any sort. Three analyses were made according to this method.†

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* For the preparation of the hydrobromic acid used, see these Proceedings, XXVIII. 17. The precipitate was assumed to contain 57.445 per cent of silver.

† After the present paper had gone to press, notice was received from Professor Mallet that Stas had suggested to him, in a letter dated January 27, 1887, a method very similar to the one just described. J. W. Mallet, Stas Memorial Lecture, p. 33. [November 12, 1893.]

RATIO OF SILVER TO BARIC CHLORIDE.

SECOND SERIES: FIRST NEW METHOD.

No. of Exp.	Corrected * Weight of Baric Chloride.	Silver weighed out.	Weight of Silver found in Filtrate.†	Weight of Silver corresponding to $BaCl_2$.	Ratio $2\,Ag : BaCl_2 = 100 : x$.	Atomic Weight of Barium.
	grams.	grams.	grams.	grams.		
35	6.36974	6.72090	0.12097	6.59993	96.512	137.419
36	5.36010	5.73383	0.18154	5.55229	96.539	137.476
37	3.92244	4.08060	0.01680	4.06380	96.522	137.440
				Average	96.524	137.445

A second new method of accomplishing the desired object consisted in the actual determination of the silver and chlorine left in a solution obtained by mixing amounts of baric chloride and argentic nitrate supposed to be equivalent.

The solution and first five wash waters filtered off from such a carefully prepared mixture, which had been shaken occasionally for about a week, were thoroughly mixed and divided exactly in half. One half was evaporated with hydrobromic acid, and the other with argentic nitrate, and the small amounts of argentic bromide and chloride were determined by reduction and the use of Volhard's method.

Subsequently it appeared that there was a slight error in the method, due to the difficulty of determining accurately such small quantities of substance. By the evaporation of solutions known to contain nothing but pure argentic chloride, it was found that the amount of silver obtained was always a little less than enough to correspond to the chlorine. Several experiments showed that the error from this cause amounted to very nearly one tenth of a milligram, hence this amount is added below to the amount of silver found in the half of the filtrates which was evaporated with hydrobromic acid.

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* For the corrections, see page 79 of this paper. These three analyses are portions of Experiments 20, 26, and 27.

† This weight, computed from the argentic bromide, has been corrected for a very slight excess of hydrochloric acid. The correction, which was of course added, amounted to 0.00026 gram in the first case, 0.00007 in the second, and 0.00009 in the third. Compare data on page 79.

RATIO OF SILVER TO BARIC CHLORIDE.

THIRD SERIES: SECOND NEW METHOD.

No. of Exp.	Corrected* Weight of Baric Chloride.	Weight of Silver taken.	Silver found in one half of Filtrate, plus correction of 0.0001 gram.	Silver corresponding to Chlorine found in the other half of Filtrate.	Corrected Silver required by Baric Chloride.	Ratio 2 Ag : $BaCl_2$ $= 100 : x$.	Atomic Weight of Barium.
	grams.	grams.	grams.	grams.	grams.		
38	4.2815	4.43558	0.00080	0.00076	4.4355	96.528	137.453
39	2.6488	2.74417	0.00063	0.00054	2.7440	96.531	137.459
40	5.9712	6.18547	0.00065	0.00118	6.1865	96.520	137.436
41	3.2841	3.40245	0.00060	0.00052	3.4023	96.526	137.449
					Average	96.526	137.449

During a large part of the considerable time consumed by these analyses, experience with the comparison of opalescence was gradually being acquired. The details of this method have been so fully given by Stas that further mention of them need not be made here. For the final experiments the baric chloride was dissolved in a large amount of water, and decomposed by a very slight excess of argentic nitrate in very dilute solution, the silver having been weighed and dissolved with the greatest care. After the mixture had been shaken occasionally for a number of days, it was allowed to settle, and two portions of twenty-five cubic centimeters each were taken out with a pipette. A little hydrochloric acid produced a more evident opalescence in one of these portions than an equivalent amount of silver did in the other, showing that too much silver had been taken. Known amounts of hydrochloric acid were therefore added very gradually to the main mass of the liquid, until, after agitation and settling, two portions of the clear supernatant liquid treated respectively with argentic nitrate and hydrochloric acid showed like intensity of opalescence. This similarity of opalescence was further confirmed by measuring the heights of parallel unknown columns of the two liquids which had been adjudged equally cloudy. From the average of a great number of readings, one could feel reasonably certain of the result within two or three per cent, corresponding to an error of not over one or two tenths of a milligram of silver in the volume of solution used.

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* The last two of these determinations formed a continuation of Experiments 28 and 29 already given, and the calculation of the amount of anhydrous baric chloride need not be repeated. The actual weight of ignited baric chloride taken in Experiment 39 was 2.64851 grams (in vacuum); but this was found to require a correction due to loss of chlorine amounting to 0.00025 grams. The corrected weight is given in the table. Since the salt used in Experiment 38 was ignited in hydrochloric acid gas, no correction was necessary. In Experiment 38 the weight of silver given in the third column is 0.00020 gram less than the amount actually weighed, because 0.20 cubic centimeter of standard hydrochloric acid was added to determine the neutrality of the baric chloride before the precipitation.

For example, in the first analysis recorded below, it was found in three preliminary trials that about 0.30 cubic centimeter of the standard hydrochloric acid should be added to the remaining mixture in order to reach the desired point. This amount was therefore added, and two portions were again taken out, treated as before, and compared.

Solution to which HCl was added.		Solution to which $AgNO_3$ was added.
9.5 c.m.	in height appeared equal to	10.0 c.m.
10.5 "	" " "	10.0 "
10.3 "	" " "	10.0 "
10.1 "	" " "	10.0 "
9.2 "	" " "	10.0 "
Average, 9.9 "	" " "	10.0 "

This average shows that the equality of cloudiness was now within the probable experimental error.

It was borne in mind, however, that a fifth of the original solution had been used up in the preliminary tests. Hence, the true amount of hydrochloric acid which should have been added to the original solution must be $\frac{5}{4} \times 0.3 = 0.375$, or practically 0.4 cubic centimeter.

Hence, since this amount of hydrochloric acid is of course a direct measure of the excess of silver originally taken, 0.4 milligram should be subtracted from the original weight.

It is needless to say that all possible care was used in these final determinations. The reiteration of the countless details would be wearisome, and hence these details are left to be inferred from what has been already written. The method is the simplest and easiest of the four; and when one has acquired experience in the comparison of opalescence, it is perhaps also the most accurate.

RATIO OF SILVER TO BARIC CHLORIDE.

FOURTH SERIES: STAS'S THIRD METHOD.

No. of Exp.	Weight of Crystallized Baric Chloride.	Weight of Anhydrous Baric Chloride.	Weight of Silver taken.	Excess of Silver found.	Total Weight of Silver.	Ratio $2\,Ag : BaCl_2 = 100 : x$.	Atomic Weight of Barium.
	grams.	grams.	grams.	milligrams.	grams.		
42	7.63356	6.50022*	6.7346	0.4	6.7342	96.525	137.448
43	12.01793	[10.23365]	10.6067	4.4	10.6023	96.523	137.442
					Average	96.524	137.445

THE ATOMIC WEIGHT OF BARIUM.

The data based upon the two more satisfactory ratios detailed in this paper have been grouped in seven series of determinations. In the first three series, including ten individual experiments upon the first ratio, the individual results are grouped together according to the condition of the baric chloride used as the starting point. This method of grouping was adopted because the analytical conditions were necessarily quite uniform, and the initial state of the salt was the most important variable. This problem having been solved satisfactorily, the accurate decision of the true end-point in the method of Gay Lussac remained the most important incidental question to be settled during the determination of the second ratio. Hence, the last four series were grouped according to the method of titration.

From the Ratio of Baric Chloride to Argentic Chloride.

	Atomic Weight of Barium if $O = 16.000$.
I. Five experiments, $BaCl_2$ ignited in air	= 137.428
II. Three experiments, $BaCl_2$ ignited in HCl	= 137.446
III. Two experiments, $BaCl_2$ not ignited	= 137.444
	137.439

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* This specimen of baric chloride was dehydrated by ignition in a stream of hydrochloric acid. The specimen whose weight is recorded in brackets below it was not ignited; but the weight of the anhydrous salt was computed by means of the proportion 7.63356 : 6.50022 = 12.01793 : x.

From the Ratio of Baric Chloride to Silver.

I. Five experiments, Stas's second method = 137.419
II. Three experiments, first new method = 137.445
III. Four experiments, second new method = 137.449
IV. Two experiments, Stas's third method = 137.445
137.440

Before discussing these averages it may be well to recall the results obtained from baric bromide. These last results may be divided into two groups of two series each, the essential difference between the two series depending upon their relative accuracy.

From the Ratio of Baric Bromide to Argentic Bromide.

I. Experiments 3 to 12; Ba = 137.424
II. Experiments 13 to 19; Ba = 137.439
137.431

From the Ratio of Baric Bromide to Silver.

I. Experiments 3 to 12; Ba = 137.422
II. Experiments 13 to 19; Ba = 137.435
137.428

Total average of four groups **137.434**

The four groups, including eleven series and forty-nine individual results, are thus essentially unanimous in the verdict that the atomic weight of barium is between 137.42 and 137.45. Upon closer examination of details, it is apparent that some of the series are more trustworthy than others. In general, the first series of each group is considerably less reliable than the following ones, for obvious reasons. The first series of the first and second groups have the additional disadvantage of having been the victims of rather unsatisfactory methods. Since the most probable errors tend in any case to lower the observed atomic weight, the striking out of these lower results appears all the more allowable.

The more trustworthy results which remain may be averaged as follows: —

From the Ratio $BaCl_2 : 2\,AgCl$; $Ba = 137.445$
" " $BaCl_2 : Ag_2$; $Ba = 137.446$
" " $BaBr_2 : 2\,AgBr$; $Ba = 137.439$
" " $BaBr_2 : Ag_2$; $Ba = 137.435$
Average **137.441**

This average is after all but little different from the total mean of all the determinations, 137.434; and either average may be taken without serious error for the atomic weight of barium. Indeed, in the present state of chemistry, the third decimal place is of little or no importance in a large atomic weight, and the round number 137.44 is sufficient for the most exacting work.

An excellent proof of the purity of the materials and the accuracy of the work is to be found in the comparison of the weights of silver and argentic chloride. Omitting in each case the less accurate first series, we may repeat the following figures:

[II.] $2\,AgCl : BaCl_2 = 100 : x = 72.6563$
[III.] $2\,AgCl : BaCl_2 = 100 : x = 72.6555$
Average 72.6559

[II.] $2\,Ag : BaCl_2 = 100 : x = 96.524$
[III.] $2\,Ag : BaCl_2 = 100 : x = 96.526$
[IV.] $2\,Ag : BaCl_2 = 100 : x = 96.524$
Average 96.5247

Hence $Ag : AgCl = 72.6559 : 96.5247$
$= 107.930 : 143.387$

Therefore the atomic weight of chlorine is found to be 35.457, a quantity exactly identical with that found by Stas in a different way. A similar comparison of the weights of the silver and argentic bromide has been given already in the fifth column in the table on page 29 of Volume XXVIII. of these Proceedings.

It remains only to compare these figures with the older ones already described. Evidently all results for barium based upon the conversion of baric chloride into baric sulphate, as well as all results including water of crystallization, are worthy of no confidence. The incomplete knowledge regarding the method of Gay Lussac manifested by Marignac and Dumas in 1858 is quite enough to explain their unsatisfactory and discrepant results. We should expect to find the ratio of baric chloride to argentic chloride the most accurately determined of all the old ratios; and in fact Turner in 1829 obtained in this way a very good result (137.45). Upon the other hand, Marignac's single result by this method (137.14) was much too low. The description of his work is so superficial that a guess as to the reason for this discrepancy is out of place; nor is such a guess necessary, for a single experiment can carry with it no important weight.

The new result for the atomic weight of barium, reduced to the various standards in present use, is given below. As before, the mathematical statement of the "probable error" is omitted, because this error is so small as to be meaningless.

If Oxygen = 16.00, Barium = 137.44
" = 15.96, " = 137.10
" = 15.88, " = 136.41